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(54) Recording medium and recording method

(57) A printing method is provided which comprises the steps of:

1. Printing with at least one ink on to a receiving material which comprises on a suitable substrate at least one ink receiving layer which comprises a particulate polymer which is characterised by a film forming temperature of between 60° C and 140° C together with at least one binder

and

2. subsequently heating and applying pressure to the printed image to fuse the polymer.

Preferably the printed image is heated by passing through a laminator. Alternatively the printed image is heated by passing through a laminator in conjunction with a second, inert releasing sheet which is held against the top surface of the print material. The second sheet may be used to produce a particular appearance to the final image such as high gloss or a security pattern. The receiving layers of the invention provide bright images after printing and fusing which show a high level of scratch and rub resistance even when wet.

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Description

Technical Field

[0001] This invention relates to a recording medium and to a method for the treatment of images produced therewith.

Background of the Invention

[0002] This invention relates to a recording medium particularly suitable to use with ink jet printers and to a method for the treatment of images prepared therewith. It particularly relates to images produced using so-called aqueous inks, that is to say inks in which water comprises the major component of the liquid phase. There is increasing interest in the use of aqueous inks for environmental and safety reasons.

[0003] Printing media suitable for use with ink jet printers are well known. Commonly these employ at least one ink-receiving layer coated on a suitable substrate. The purpose of the ink-receiving layer is to take up the ink rapidly and improve image quality. One problem with images produced using aqueous inks is that they can be insufficiently robust to handling, and that the image or the ink-receiving layer on which it is printed is sensitive to rubbing and scratching. In addition the printed image frequently becomes more sensitive to handling and damage under damp conditions, and can sometimes be washed completely away.

[0004] Several methods of overcoming the poor robustness of images produced using aqueous inks are known. For instance various additional coatings and treatments for ink receiving layers have been proposed, such as lacquers or varnishes which have to be applied after printing the image, thus requiring additional equipment. For instance Patent Application GB 2'337'482 provides a method for increasing the rub resistance of an image by coating or overprinting the image with an aqueous solution of a styrene acrylate polymer.

[0005] Another method of improving the robustness of printed images is to laminate or encapsulate them, and this is particularly common when they are intended for external display. By lamination is meant the combination of a printed image with a transparent overlay, this combination usually being accomplished with an adhesive activated by heat, pressure or both. The overlay acts as a physical protection for the image and completely seals it from ingress of water. By encapsulation is meant the combination of a printed image layer between two laminating sheets, that on the image surface being transparent, the combination being accomplished with an adhesive activated by heat, pressure, or both. Encapsulation is most effective if the laminating sheets extend beyond the printed image and are bonded to each other at the extremities, thus preventing ingress of water through exposed edges of the image.

[0006] However lamination and encapsulation are both expensive because additional materials are required together with additional handling and equipment, and there is considerable interest in finding a cheaper and simpler method of increasing the robustness of images produced using aqueous inks.

[0007] As an alternative to lamination or overprinting, Patent Applications JP 59-222'381, JP 07-237'348, JP 08-02'090, 09-104'164, EP 0'858'905 and EP 0'858'906 disclose a heat seal method of protecting an ink jet image wherein the receiving system comprises two layers coated on a suitable base. The lower layer is an ink-receiving layer, which is absorbent to the ink, whereas the upper layer comprises a film-forming polymer in a binder. After printing the upper layer may be sealed by heating to form a robust barrier to protect the image in the lower layer. This is similar to laminating the image, but does not require the additional expensive lamination sheet.

[0008] However this heat seal method needs to achieve high temperatures to seal the image (temperatures up to 170° C are mentioned in the examples of Patent Application EP 0'858'906) and also requires a relatively complicated and expensive receiving sheet.

[0009] Various ink receiving materials which comprise a combination of a particulate polymer and a hydrophobic binder are already known. For instance Patent US 3'968'319 discloses a particulate polymer for use in paper coatings, Patent US 4'196' 253 discloses a paper coated with a binder and organic particles, Patent US 4'371'582 discloses an ink jet recording sheet containing a basic latex polymer, Patent US 4'442'247 discloses a coating composition comprising a combination of an aqueous resin with an insoluble resin, Patent US 4'686'118 discloses a recording medium wherein the coating comprises a combination of a hydrophilic and a hydrophobic polymer, Patent US 5'102'731 discloses a recording medium wherein the coated layer comprises a hydrophilic urethane resin and fine organic or inorganic particles, Patent US 5'254'403 discloses a coated recording sheet wherein the receiving layer comprises a mixture of a latex polymer with two hydrophilic polymeric binders, Patent US 5'270'103 discloses a receiver sheet coated with a coating comprising a pigment, a binder and a latex polymer, Patent US 5'405'678 discloses a coating comprising a latex polymer which has not been completely coalesced, Patent US 5'672'392 discloses a process for preparing ink jet recording materials whereof the coatings comprise starch, an insoluble copolymer and a binder, Patent US 5'714'235 discloses an ink jet recording sheet containing casein and a styrene-butadiene rubber, Patent US 5'925'712 discloses a fusible printable coating wherein one of the alternative compositions comprises a combination of a powdered thermoplastic polymer and a binder, and Patent Applications JP 59-204'591 and JP 59-204'592 disclose ink jet receiving coatings which comprise microcapsules which are ruptured after printing to improve the robustness of the image.

[0010] There is thus still a need for an imaging medium and method which will provide images resistant to washing and handling when printed using aqueous inks without lamination. We have found a medium and a method, which achieves these objectives.

Summary of the invention

[0011] According to the present invention there is provided a printing method which comprises the steps of:

1. Printing on to a receiving medium which comprises on a suitable substrate at least one ink receiving layer which comprises a particulate polymer which is characterised by a film forming temperature of between 60° C and 140° C, preferentially from between 100°C and 120° C, together with at least one binder

and

2. Subsequently heating and applying pressure to the printed image to fuse the polymer.

[0012] The method and recording media of the invention are much simpler than previously known heat sealing recording media and methods for printed images because the ink receiving layers may consist of only a single ink receiving layer rather than the minimum of two known previously, and is thus considerably simpler and cheaper to manufacture. The ink receiving layers of the invention provide bright images after printing and fusing which show a high level of scratch and rub resistance even when wet.

Detailed Description of the Invention

[0013] Suitable substrates to carry the layer or layers of the invention include any of those commonly used for printing and imaging media, for example paper, high wet-strength paper, tracing paper, heavyweight paper, card, cardboard, label grade paper, treated paper such as resin or polyethylene coated paper, pigmented paper, synthetic papers, canvas, cloth, fabric, metals such as aluminium, polymeric substrates such as cellulose acetates, polyethylene, polypropylene, polyvinyl chloride, polyesters including poly(ethylene terephthalate) and poly(ethylene naphthalate) and transfer materials.

[0014] Preferably the binder is a hydrophilic binder. Suitable hydrophilic binders include gelatine, polyvinyl alcohol, polyvinyl pyrrolidone, copolymers of polyvinyl alcohol, carbohydrates, treated carbohydrates, gums such as tragacanth gum, modified carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, acrylic polymers, casein, starch, polyethylene imine, and mixtures thereof.

A particularly suitable hydrophilic binder is polyvinyl alcohol. It is to be understood that commercial samples of polyvinyl alcohol are normally prepared by hydrolysis of polyvinyl acetate, and that this hydrolysis does not always go to completion. Thus a preferred hydrophilic binder is polyvinyl alcohol, which has a degree of hydrolysis of at least 90 %, and a particularly preferred binder is polyvinyl alcohol, which has a degree of hydrolysis of about 99 %. This is hereinafter referred to as 99 % PVA.

[0015] Suitable polymers for the particulate polymer include polyethylene and copolymers of ethylene with other ethylenically unsaturated monomers, such as acrylate monomers. A suitable particle size for the particulate polymer is between about 1 μm and about 50 μm, with a particle size between about 5 μm and about 20 μm being preferable. A suitable particulate polymer comprises polyethylene particles of random shape and particle size of about 25 μm.

A particularly preferred particulate polyethylene polymer comprises low-density polyethylene particles having an average diameter of approximately 25 μm.

Another suitable particulate polymer comprises particles of a 7 % acrylic acid / polyethylene copolymer having an average diameter of about 10 μm.

These polymers have crystalline melting points of 105° C - 107° C.

[0016] A suitable coating weight for the ink-receiving layer is from about 5 g/m^2 to about 50 g/m^2. A preferred coating weight for the receiving layer is from about 20 g/m^2 to about 40 g/m^2. The ratio of the coating weight of the particulate polymer to that of the hydrophilic binder may be from about 20 : 1 to about 1 : 1, but preferably is between about 10 : 1 and about 5 : 1.

[0017] The receiving layer may advantageously also comprise additives which are commonly added to ink receiving layers such as surfactants to improve coating quality, cross linking agents, optical brightening agents, inorganic pigments or fillers such as chalk, silica, alumina, kaolin and the like, light stabilisers, biocides, and dye fixatives such as the polymers provided by Patents US 5'342'688, US 5'589'269 and US 5'712'027. Suitable cross linking agents for the preferred polyvinyl alcohol binders of the invention include aldehydes such as glyoxal, boric acid, polyethylene imines and divalent metallic cations.

[0018] According to a preferred aspect of this invention, the printed image is heated by passing through a laminator. By laminator is meant a device which is normally used for the lamination of printed images which comprises a means of heating and pressing together the image and the laminating sheet thus causing the two to adhere, commonly by passing them through a nip between a pair of heated rollers. This aspect is particularly preferable because many printing and processing houses already possess and use laminators, which can be applied to the materials of this invention. However the advantage of this invention is that the additional expensive lamination sheet is unnecessary.

[0019] According to another aspect of the invention, the printed image is heated by passing through a laminator in conjunction with a second, inert sheet, which is held against the image protective layer of the material. The inert sheet does not adhere to the material, but protects it from the rollers of the laminator. Moreover the

use of a smooth inert sheet will impart a high gloss or other desired appearance to the final image. Alternatively a suitable choice of the inert sheet may be used to produce a pattern such as a security symbol after contacting with the image. The inert sheet may then be recycled almost indefinitely.

[0020] The method and recording media of the invention are particularly suited to the treatment of images produced using ink jet printers. Aqueous inks are commonly used in such printers, particularly those designed for use in the home or office, but the invention is also suitable for ink jet printers using non-aqueous inks such as those based on mineral oils and organic solvents. Ink jet printing is a non impact printing method that in response to a digital signal produces droplets of ink that are deposited on a substrate to produce an image. Ink jet printing has found broad application in recent years. Any convenient ink jet printer may be used, for example a continuous printer or a piezoelectric or thermal drop-on-demand printer.

[0021] The invention may also be used with other printing methods such as flexographic printing, with pen type plotters, or with marker pens and the like. Suitable colorants for the inks include dyes or pigments. Preferred inks for the invention are pigmented aqueous inks.

[0022] The media and method of this invention are suitable for many uses where robustness of an ink jet image is important, such as posters, banners, displays, labels, and the like. The method of this invention is also particularly suitable for use with a wide variety of packaging materials, e.g. heavy weight paper, card or cardboard.

[0023] The media and method of this invention are also particularly suitable as a security printing system, and this aspect of the invention is especially preferred. After the material has been sealed by heating it is no longer receptive to inks, and is thus difficult to alter and offers high levels of protection from fraud and forgery. In an additional aspect of the invention when it is used as a security printing system, a suitable mark or pattern such as, for example, a holographic pattern may be embossed on or transferred to the image at the heating stage. This pattern may be carried on the inert sheet used in contact with the image during the heating stage, or may be carried on a roller or stamp used in contact with the image at the heating stage.

However the method of this invention is novel and the coatings are particularly suitable for the method.

Examples

[0024] The following examples will serve to illustrate the invention:

Example 1

[0025] A formulation was prepared using the components of Table 1:

Table 1

Polyvinyl alcohol (10 % solution)	40.0 g
Silicone surfactant	0.2 g
Ethylene acrylic acid copolymer beads	25.0 g
Optical Brightening Agent	0.2 g
Deionised water	34.6 g

[0026] This formulation was coated on to a subbed polyvinyl chloride substrate to give a coating weight of 25 g/m^2. An image was printed with pigmented inks using a Novajet III printer, and the printed coating was passed through a GBC 1200 laminator at a heat setting corresponding to a temperature of 120° C together with a piece of paper to seal the image. The paper was removed leaving a smooth clear glossy image, which was resistant to wet rubbing.

Example 2

[0027] A formulation was prepared using the components of Table 2:

Table 2

Polyvinyl alcohol (10 % solution)	400 g
Silicone surfactant	2 g
Polyethylene beads	250 g
Deionised water	348 g

[0028] The polyvinyl alcohol used was a commercial sample from Harco under the trade name Mowiol 28-99 having a degree of hydrolysis of 99 %. The surfactant was from BYK Chemie under the trade name BYK 348. The polyethylene beads were low-density polyethylene spherical beads having an average diameter of about 12 µm available under the trade name EA209 from Sumitomo. The formulation was coated on to a substrate comprising plain paper having a substance of 80 g/m^2 to give a wet coating weight of 100 g/m^2, approximately 29.2 g/m^2 when dry. An image was printed with pigmented inks using a Novajet III printer, and the coating was passed through a GBC 1200 laminator at a heat setting corresponding to a temperature of 115° C with the image surface in contact with a piece of clear film to seal the image. The film was removed leaving a smooth clear glossy image, which was resistant to wet rubbing.

Example 3

[0029] A formulation was prepared using the components of Table 3:

Table 3

Polyvinyl alcohol (10 % solution)	400 g
Silicone surfactant	2 g
Polyethylene particles	250 g
Deionised water	348 g

[0030] The polyvinyl alcohol used was a commercial sample from Harco under the trade name Mowiol 56-98 having a degree of hydrolysis of 98 %. The surfactant was from BYK Chemie under the trade name BYK 348. The polyethylene particles were low-density polyethylene particles of random shape and average particle size about 25 μm available under the trade name Coethylene HX1681 from Du-Pont. The formulation was coated on to a substrate comprising plain paper having a substance of 80 g/m^2 to give a wet coating weight of 100 g/m^2, approximately 29.2 g/m^2 when dry. An image was printed with pigmented inks using a Novajet III printer, and the printed coating was passed through a GBC 1200 laminator at a heat setting corresponding to a temperature of 115° C with the image surface in contact with a piece of clear film to seal the image. The film was removed leaving a smooth clear glossy image, which was resistant to wet rubbing.

Claims

1. A printing method, which comprises the steps of:
   1) Printing on to a receiving medium which comprises on a substrate at least one ink receiving layer which comprises a particulate polymer which is characterised by a film forming temperature of between 60° C and 140° C together with at least one hydrophilic binder
   and
   2) subsequently heating and applying pressure to the printed image to fuse the particulate polymer.

2. A method according to claim 1 wherein the image is heated using a laminator.

3. A method according to claim 2 wherein the image is heated in contact with an inert sheet.

4. A method according to any one of claims 1 to 3 wherein the substrate is selected from the group consisting of paper, high wet-strength paper, tracing paper, heavyweight paper, card, cardboard, label grade paper, treated paper, pigmented paper, resin coated paper, polyethylene coated paper, synthetic papers, canvas, cloth, fabric and transparency materials such as cellulose acetate, polyethylene, polypropylene, polyvinyl chloride, poly(ethylene terephthalate) or poly(ethylene naphthalate).

5. A method according to any one of claims 1 to 4 wherein at least one binder is selected from the group consisting of gelatine, polyvinyl alcohol, polyvinyl pyrrolidone, carbohydrates, gums, treated carbohydrates such as hydroxyethyl cellulose or carboxymethyl cellulose, acrylic polymers, casein, starch and mixtures thereof.

6. A method according to any one of claims 1 to 4 wherein at least one binder is polyvinyl alcohol or gelatine.

7. A method according to any one of claims 1 to 6 wherein the particulate polymer is polyethylene or a copolymer of ethylene with an acrylate.

8. A method according to any one of claims 1 to 6 wherein the particulate polymer comprises low-density polyethylene particles having an average particle size of approximately 25 μm.

9. A security printing method according to any of claims 1 to 8 wherein a security mark is embossed on the image at the heating stage.

10. A recording medium for ink jet printing comprising a substrate coated with at least one ink receiving layer comprising a particulate polymer having a film forming temperature between 60° C and 140° C together with at least one hydrophilic binder.

11. A recording medium according to claim 10, wherein said substrate is selected from the group consisting of paper, transparency materials, synthetic papers, canvas, cloth, fabrics, transfer materials and polymeric substrates.

12. A recording medium according to claim 11, wherein said paper is selected from the group consisting high wet-strength paper, tracing paper, heavyweight paper, card, cardboard, label grade paper, treated paper, pigmented paper, resin coated paper, polyethylene coated paper and synthetic paper.

13. A recording medium according to claim 10, wherein said ink receiving layer includes at least one binder selected from the group consisting of gelatine, polyvinyl alcohol, polyvinyl pyrrolidone, carbohydrates, gums, treated carbohydrates, hydroxyethyl cellulose, carboxymethyl cellulose, acrylic polymers, casein, starch and mixtures thereof.

14. A recording medium according to claim 13, wherein said ink receiving layer includes comprises polyvinyl alcohol having a degree of hydrolysis of at least 90 %.

15. A recording medium according to claim 10, wherein said particulate polymer has a particle size between 1 μm and 50 μm.

16. A recording medium according to claim 10, wherein said particulate polymer comprises low-density polyethylene particles having an average particle size of approximately 25 μm.

17. A recording medium according to claim 10, wherein said ink receiving layer has a coating weight from 5 g/m^2 to 50 g/m^2.